

A MICRO GAS PRECONCENTRATOR WITH IMPROVED PERFORMANCE FOR POLLUTION MONITORING AND EXPLOSIVES DETECTION

E. H. M. Camara^(1, 3), P. Breuil*⁽¹⁾, D. Briand⁽²⁾, N. F. de Rooij⁽²⁾, C. Pijolat⁽¹⁾

⁽¹⁾ Ecole Nationale Supérieure des Mines, Centre SPIN, LPMG-UMR CNRS 5148, 158
Cours Fauriel, 42023 Saint-Etienne, France

⁽²⁾ Ecole Polytechnique Fédérale de Lausanne, Institute of Micro-Engineering,
Rue Jaquet-Droz 1, P.O. Box 526, CH-2002 Neuchâtel, Switzerland

⁽³⁾ Faculté des sciences, Université de Neuchâtel,
Avenue du 1^{er} mars, 26, CH-2002 Neuchâtel, Switzerland

*Corresponding author : P. Breuil, Phone 33 4 77 42 01 51, Fax 33 4 77 49 36 20, pbreuil@emse.fr

Abstract: This paper presents the optimization of a micro gas preconcentrator based on a micro-channel in porous and non-porous silicon filled with an adequate adsorbent. This micro gas preconcentrator is both applicable in the fields of atmospheric pollution monitoring (Volatil Organic Compounds-VOCs) and explosives detection (nitroaromatic compounds). Different designs of micro-devices and adsorbent materials have been investigated since these two parameters are of importance in the performances of the micro-device. The optimization of the device and its operation were driven by its future application in outdoor environments. Parameters such as the preconcentration factor, cycle time and the influence of the humidity were considered along the optimization process. As a result of this study, a preconcentrator with a total cycle time of 10 minutes and the use of single wall carbon nanotubes (SWCNTs) as adsorbent exhibits a good preconcentration factor for VOCs with a limited influence of the humidity. The benefits of using porous silicon

to modify the gas desorption kinetics are also investigated.

KEYWORDS

Gas preconcentrator, Micro-channel, Porous silicon, Carbon nanotubes, Adsorbent

1. INTRODUCTION

In miniaturization of physical analysis methods, preconcentration appears as the essential element for improving both the sensitivity and the selectivity of these devices^[1, 2, 3, 4, 5]. Thus, micro-preconcentrators find their applications in various systems for gas analysis such as solid phase micro gas chromatography (μ -GC)^[6, 7, 8, 9, 10], ion mobility spectrometry (IMS)^[11, 12, 13] and electronic nose (E-nose)^[14, 15, 16, 17].

The use of detection systems based on the preconcentration is growing since the need to quantify very low concentration is growing up as well as in the field of civil security as in agribusiness and healthcare. For example, in the later, there is a demand of preconcentrators for medical diagnostics as addressed by Mr. Cho Seong et al^[17] and William A. Groves et al^[18]. They have analyzed through a preconcentration system, the air exhaled by a patient while knowing that the appearance of some gas molecules in exhaled air is characteristic of the metabolism, thus the state of patient's health. The presence of some of these VOCs is attributed to a definite disease; for example, alkanes, benzene derivatives o-toluidine and aniline are referred to lung cancer, while acetone is linked to diabetes...

In the environmental field, it should be noted that the increasing of industrialization around some major cities causes great vigilance in the monitoring environmental pollution and the prevention of disasters. Each country, through an environmental quality agency, sets tolerance limits for some VOCs. For example, in United States, the threshold for benzene is determined by the U.S. EPA (U.S. Environmental Protection Agency) to 500ppb in ambient air and 5ppb in drinking water^[19]. While in France, the limit is set by IFEN (French Institute of Environment) to $10\mu\text{g}/\text{m}^3$ ^[20]. These limits continuously being reviewed to lower levers require the implementation of more performing detection equipments with a low detection limit and very short sampling time.

The need to improve both the sensitivity and the selectivity of some detection systems has prompted many laboratories to review the implementation of their gas pre-conditioning system. Thus, systems with

multiple stages of preconcentration were developed to reduce both the influence of water vapor and other interfering gases such as alcohol derivatives ^[17, 21]. S. M. Cho et al ^[17] have implemented two-stage preconcentrators filled with a hydrophobic adsorbent (carbotrap) allowing to reduce the influence of water vapor in the analysis of human exhaled breath. There are also other multiple stages preconcentration techniques based on the difference of desorption temperature between the two preconcentration units to overcome the influence of other interfering gases upon detection as demonstrated by B. Alfeeli et al ^[21] in their concept of cascaded micro-preconcentrator.

A new innovative process in the field of micro-preconcentration is the use of porous silicon. Indeed, the use of porous silicon as a binding surface for filling adsorbent appears as a very attractive approach in the development of miniaturized preconcentration because it offers the possibility to deposit by fluidic solution various types of adsorbent while avoiding the problems of overpressure during the experiences.

In our previous study ^[22 23, 24], a gas pre-concentrator based on porous silicon micro-channels filled with carbon nanopowders from a fluidic solution has been developed. The present work aims to improve the performance of this device, with new approaches in the design as well as in the choice of adsorbent materials and modes of operation. We have further investigated the contribution of porous silicon in the adsorption and desorption phases since besides the increase of its specific surface area as reported in ^[26], porous silicon when coupled with the adequate adsorbent can also modify the desorption kinetics of the target gas.

Alternative absorbent materials such as carbon nanotubes and polymers, whose surface areas, pores-size distributions, and structures can be varied to serve as conformal adsorbents, were evaluated for the improvement of the performance of the preconcentrator ^[5].

The devices in this study have been developed targeting the preconcentration of benzene and nitrobenzene which are representative gases for several types of applications relevant from atmospheric pollution control to explosives detection.

2. EXPERIMENTAL

2.1. Adsorbent Materials

The choice of the adsorbent material is an important factor in the performance of a micro gas preconcentrator. The suitable adsorbent must have a strong affinity with the target gas, a low activation energy of desorption, a large adsorption capacity vis-à-vis of the target gas and finally a good binding of its particles on the preconcentrator substrate in order to avoid an evacuation of the deposited adsorbent under high gas flow which is harmful for the performance of the devices. The activation energy of the adsorbent is symbolized by its desorption temperature; while the adsorption capacity is linked to the specific area.

Therefore, four different adsorbents such as activated carbon, carbon nanotubes (Single Walled Carbon NanoTubes-SWCNTs, Multi Walled Carbon NanoTubes-MWCNTs) and Tenax polymer have been tested for the preconcentration of benzene and nitrobenzene in presence of humidity by using various techniques: BET (Brunauer, Teller and Emmett) method, Thermal Programmed Desorption (TPD) and applying them to micro-preconcentrator devices.

The BET method is a volumetric adsorption of gas point by point, which allows obtaining the complete isotherms (adsorption and desorption). These gas adsorption/desorption isotherms (Nitrogen, Argon, Krypton...) will permit the determination of the specific area and the adsorbent texture. The value of the specific area is obtained from the absorption isotherms of a gas at the liquid nitrogen temperature (77K). TPD technique is often used to discern the different desorption products of a given adsorbent after an adsorption phase. This technique consists in programming the desorption heating rate and selectively measuring the desorption products with a mass spectrometer. In some cases, the adsorption phase can be done in situ and the desorption heating rate is set to 100°C/min in order to make easier the discrimination of the various desorption products.

The carbon adsorbent used in this test has been activated by thermal process. The activation of carbon is an oxidizing reaction in order to release internal porosity created during the carbonization, to expand the pores, to create new micropores and to increase its specific area. This step must be controlled to avoid the total elimination of the carbon structure as the activation at high temperature (up to 900°C) under oxygen can cause the total disappearance of carbon structure. That is why we have done the activation of carbon

nanopowder at 500°C during 3 hours in presence of oxygen. All the others adsorbents materials were not activated because this process was not needed due to of their specific area already higher.

2.2. Preconcentrator

Micro-devices with different designs have been fabricated (figure 1) by deep reactive ion etching (DRIE) of silicon wafers using a thick photoresist mask. In the case of porous silicon channels, prior to the DRIE, a silicon nitride film is deposited to act as a masking layer during the porous silicon formation. Then, for both types, a 50 nm thick thermal oxide of is grown prior to their sealing with a glass cover by anodic bonding. The different channels are designed with the necessity of having some pillars or walls within the channels in order to control the powders deposition by fluidic solutions ^[23, 24]. The neutral microchannel is designed without structures in the internal chamber while the zigzag design with channel system at inlet/outlet, mostly used in this work, is made with "V" shaped structures in order to improve the flow distribution not only during the adsorbent deposition but also during experiments.

The first micro-devices realized at the beginning of this study were made following two depths of etching. The internal chamber etched at 120µm into the silicon contains parallel channels, either smooth or with the "scales". In order to receive the metallic micro-capillaries of 350µm used as fluidic connectors, the inlet and outlet of the device were etched to a depth of 325µm. But we faced a non-uniform distribution of flow (Figure 1) and overpressure during the experiments, which have been confirmed by some fluidic simulations done under three hypotheses such as:

- The pressure is applied only in the entrance of the microdevice while the outlet is under atmospheric pressure;
- No interaction between the substrate and the fluid except the friction forces;
- And the turbulence effect was not considered in this simulation model.

New micro-components were designed with a uniform depth of 325µm for both the inlet/outlet and the internal chamber in order to compensate the overpressure observed on previous devices during tests. In addition, inlet and outlet were fabricated with a channel system to promote a uniform distribution of fluid unlike the old micro-components. Indeed, the latter did not have this channel system and we observed for them a non-uniform distribution of flow when performing the fluidic simulation developed below.

This improvement in the design of the micro-channels was confirmed by series of simulation devoted to new micro-devices which have pointed, on one hand, an improvement in the distribution of the gas flow with the presence of channel system at the inlet/outlet of the micro-devices (Figure 1) and on other hand, a reduction of pressure losses thanks to the uniform depth of 325 μ m through all the microchannel in this new design.

2.3. Adsorbent deposition

The adsorbent insertion in micro-channels has been realized by two methods. The first one is a deposition using a fluidic solution ^[24], and the second one consists to deposit the adsorbent in a paste form before the sealing of the glass cover. The choice of the deposition method is closely related to the adsorbent nature. According to dimension of the metallic capillary used as fluidic connection (220 μ m of internal diameter), the first deposition method is more suitable for adsorbent materials with a particle size less than 5 μ m of external diameter. Thus, the activated carbon (100nm of particle size) and carbon nanotubes (CNTs) were inserted in the microchannels by fluidic solution while Tenax TA was deposited in a paste form before the sealing of the microdevices because of its large particle size close to 250 μ m.

These experiments on the fluidic deposition of the adsorbent have shown that the presence of pillars in the preconcentration chamber, particularly in the “zigzag” design, is a key factor to homogenize the distribution of the liquid flow through the entire device and to enhance the carbon deposition. It was observed that the use of porous silicon has increased the quantity of deposited carbon in the micro-channels. In fact, the presence of pores on the surface of the walls constitutes an important asset to get a good binding layer and thus to increase the quantity of adsorbent filled in the micro-channel compared to non-porous silicon ^[23].

Once the devices filled with adequate adsorbent material, the fluidic connections are made with metallic capillaries (steel) having 220 μ m of internal diameter. The capillary is filed, partially introduced in the device and then fixed with a ceramic cement in order to not block the connectors during the sealing.

2.4. Heating element

In order to have an autonomous component, for either the thermal treatments of the adsorbent materials and the desorption of the trapped gases, a platinum heater is integrated on the backside of the device by

screen printing and the electrical connections are made with gold wires pasted on a platinum lacquer. This heating element is used to heat the device at temperatures up to 500°C with a very homogeneous distribution of the temperature considering the good thermal conductivity of the silicon, as it was reported in our previous works ^[23, 24]. To have a good regulation of temperature, the micro-preconcentrator is suspended in a metallic box (Figure 2).

2.5. Optimization of the experimental parameters

Five main parameters are of importance for the optimum operation of a preconcentrator device with a given geometry and filled with a fixed quantity of specific absorbent material: the gas flow rate during the gas adsorption, the gas flow rate during the desorption phases, the heating rate during the gas desorption phase, the duration of the gas adsorption and desorption phases, and the gas volume of the detector.

The miniaturization of such device imposes us a limitation on the gas flow rate, but for preconcentration, high flow rates are preferred during the adsorption in order to increase the desorption peak amplitude for a given time of adsorption. The adsorption phase flow was set at 167mL/min, which allowed us to inject a significant quantity of pollutant in a short time, while the desorption phase flow was maintained at 33mL/min to avoid an important dilution of the desorbed quantity. Likewise, to avoid a considerable detection volume, the metallic capillary at the outlet of our micro-preconcentrator was directly connected to the inside of the detector through its packaging (Sensor from FIGARO ref. 2620), and the latter was then calibrated in order to correct the influence of the gas flow on the characteristics of its response ^[23]. Otherwise, some experiments were initially made with a miniaturized sub ppm PID (Photo Ionization Detector, RAE ppb).

Since the maximum of the desorption peak is an increasing function of the heating rate ^[23], the preconcentration tests were performed with a heating rate of 160°C/min, which corresponds to the maximum rate that can reach the heating resistance deposited on the backside of the micro-channels. the maximal temperature is 350°C.

Finally, the increase of the adsorption time can lead to an enhancement of the desorption peak amplitude, but in the same time causes a longer preconcentration cycle which for some applications might not be desirable. Therefore, the adsorption and desorption times were maintained constant all through the

experiments and lasted for 5 minutes since for these targeted applications as the pollution monitoring, a short preconcentration cycle is more appropriate.

So, it is very difficult to define a preconcentration factor since, for a given preconcentrator, the “amplification” of the concentration is closely related to the duration of the gas adsorption phase, the flowrates during adsorption and desorption phases, and the heating rate. However, we will measure a “practical” preconcentration factor which we defined as the ratio between the maximum of the measured concentration during the desorption phase and the concentration of the injected gas.

3. RESULTS AND DISCUSSIONS

3.1. Specific area measurement

The first tests were especially dedicated to the measurement of the specific area of the selected adsorbent materials namely carbon nanopowder, carbon nanotubes (SWCNTs, MWCNTs) and a polymer (Tenax TA) by nitrogen adsorption using the BET method. These results show that the specific area of the activated carbon nanopowder and the SWCNTs nanotubes are higher than the one of the three other adsorbents (Table 1).

However, a large specific surface does not mean necessarily a large adsorption capacity because the latter is closely related to the degree of affinity between the adsorbent and adsorbed gas. So the best solution is to evaluate the adsorption capacity of these adsorbents towards to benzene and nitrobenzene.

3.2. Benzene adsorption

3.2.1. Thermal Programmed Desorption (TPD)

The second series of experiments concerned the evaluation of the adsorption capacity of the adsorbents by TPD technique coupled with a mass spectrometer.

The adsorption capacity for benzene of the four adsorbents has been evaluated in similar conditions and in the presence of humidity obtained by bubbling the gas in a bottle of water at ambient temperature. On the one hand, there is a significant desorption peak of water with the activated carbon nanopowder unlike the

three other adsorbents which have a low affinity with water vapor (Figure 3). This result reflects a higher decrease of the adsorption capacity of the activated carbon nanopowder in a presence of water, which is very harmful for the experimentation in ambient air. On the other hand, the benzene desorption peak obtained with the activated carbon nanopowder and SWCNTs is about 5 times higher than the one obtained with MWCNTs and Tenax TA. This demonstrates a strong affinity of these two compounds with benzene since the same adsorbent mass has been used for these TPD experiments (Figure 4, 5 and 6).

However, it should be noted that the temperature of the maximum of the desorption peak amplitude varies with the adsorbent material. It is estimated at about 120, 180, 280 and 490°C respectively for Tenax TA, activated carbon nanopowder, SWCNTs and MWCNTs, respectively. The high desorption temperatures of the MWCNTs manifest an important activation energy of the desorption synonym with a strong link between the adsorbent and adsorbed gas which is bad for the reduction of the power budget and also for the reliability of the device. Therefore, we decided to not use MWCNTs for the following experiments. It should be noted too secondary benzene peaks between 400 and 600°C, probably due to other sites and mechanisms of adsorption-desorption.

TPD experiments performed with carbon nanopowder deposited on porous and nonporous silicon have shown that the benzene kinetics of desorption on carbon is closely linked to the substrate nature on which the carbon is deposited. Indeed, the desorption temperature of benzene adsorbed on carbon deposited on porous silicon substrate (200°C) is about 60°C lower than the one obtained with a non-porous silicon substrate (260°C) (Figure 7).

3.2.2. Experiments with the micro-preconcentrator

Following the conclusions drawn from the previous TPD experiments presented in the sections above, the preconcentration tests have been performed on silicon and porous silicon micro-channels with a “zigzag” design. In order to study in similar conditions the effect of optimized parameters, the quantity of deposited adsorbent on all micro-channels will be equal to about 1mg.

On one hand, the tests of these porous silicon micro-channels with carbon deposition have shown that the porous silicon, besides increasing the quantity of deposited carbon, contributes to the effectiveness of the gas preconcentration by making the desorption easier and thereby reducing the desorption temperature and at last the duration of the preconcentration cycle (Figure 8).

This complete desorption of the couple porous silicon-carbon is, maybe, due to its activation energy of desorption lower than the one for the pair non-porous silicon-carbon. The maximum of concentration obtained during desorption is about 15 ppm corresponding to a “practical” factor of preconcentration (as defined above) of about 60.

On other hand, the preconcentration tests of the non porous silicon micro-channels filled with SWCNTs have shown that the influence of water vapor in the performance of the micro-preconcentrator is lower than the one filled with activated carbon nanopowder, for which the sensor response during the desorption is intensely reduced in presence humidity (Figure 9, 10).

However, it should be noted that the desorption parameters of the non porous silicon micro-channels filled with SWCNTs are not optimum since we have observed a low factor of preconcentration and a spread of its desorption peak, which is synonym of a insufficient both heating rate (160°C/min) and desorption temperature (240°C). Some experiments are underway to optimize the preconcentration characteristics of the device when using SWCNTs.

The other experiments under benzene with SWCNTs and Tenax TA are summarized in the table 2 have shown firstly, the interest of using SWCNTs for reducing of the influence of water vapor during the adsorption phase and secondly, the low desorption temperature when Tenax is used as adsorbent material in opposition of the activated carbon.

Others VOCs with high saturation vapor pressure such as xylene have been tested with our micro-preconcentrator and the results are shown in the table 2. They confirm the interest of using Tenax for these typical VOCs.

3.3. Nitrobenzene adsorption

3.3.1 Thermal Programmed Desorption

These TPD experiments with nitrobenzene adsorption have shown a strong link between the nitrobenzene molecules and carbon nanopowder particles making thereby the desorption more difficult. Indeed, there is a low desorption of nitrobenzene at 200°C and a high desorption of benzene is observed meaning thus the decomposition of nitrobenzene molecules in benzene at above 300°C (Figure 11). Unlike carbon, the polymer Tenax TA released easily nitrobenzene molecules during the desorption at a temperature below 150°C and no decomposition of the latter is observed since the benzene desorption peak is very small compared to nitrobenzene peak (Figure 12).

3.3.2. Experiments with the micro-preconcentrator

Tests under nitrobenzene realized with a micro-preconcentrator have confirmed that the nitrobenzene molecules are strongly adsorbed on the carbon adsorbent making thus the desorption quasi impossible. As shown in the Figure 13, after a cleaning step at 200°C followed by an injection of 1ppm of nitrobenzene during 120min, no nitrobenzene is desorbed even with a temperature of about 200°C.

In addition, when this experiment has been performed again by heating the micro-preconcentrator until 350°C during one hour, only a small amount of nitrobenzene is desorbed. While the Tenax, after a cleaning step at 150°C followed by an injection of 1ppm of nitrobenzene, a total desorption of the target gas is observed only at 120°C before the end of the heating confirming therefore the TPD observations (Figure 14).

3.4. Summary and perspectives

All these tests experimented with our micro-preconcentrator have shown that the efficiency of the latter is closely related not only to the adsorbent material but also to the nature of the micro-preconcentrator substrate on which the test has been done. Therefore, the table 2 summarizes the results obtained with our

micro-preconcentrator with respect to the adsorbent, the nature of the substrate and the target gas. The preconcentration of nitrobenzene with macroporous silicon microchannel filled with carbon adsorbent (symbolized by the question mark) has not been done yet. It will be an interesting test in order to confirm the reduction of the desorption temperature of the nitrobenzene easing thus the use of carbon material for the preconcentration of nitroaromatic gases deriving from explosive compounds.

Another idea now is to reduce the dimension of the microchannel because at the beginning of this project, we opted for a large deposit of adsorbent in the micro-device but over time we realized that for the detection of trace VOCs (concentrations of hundreds of ppb), few milligrams of carbon are efficient to perform these experiences. Therefore, reducing the size of micro-component seems necessary, firstly, to obtain a more compact deposit of the adsorbent promoting interstitial porosity, more uniform distribution of the flow and secondly, to improve the thermal inertia because of its small size (Figure 15).

4. CONCLUSIONS

The effect of gas preconcentration in micro-channels has been demonstrated following a preliminary optimization of both the microchannel designs and the operating parameters. The use of four different adsorbent materials has been evaluated in a presence or not of relative humidity. To this end, SWCNT appears as adequate adsorbent for preconcentration of benzene in presence of humidity because of its high specific area and adsorption capacity and its low affinity with water vapor. While Tenax TA polymer seems the ideal candidate for the preconcentration of nitrobenzene since the latter is completely desorbed below 150°C.

Another important result of this study is the development of micro-preconcentrator on porous silicon. In fact, the porous aspect of the micro-preconcentrator substrate contributes to increasing the quantity of adsorbent filled by fluid through the micro-device. Besides this, it facilitates the desorption of gas molecules adsorbed on the adsorbent deposited on it by reducing the temperature of desorption of adsorbent-

adsorbate couple. This advantage can also make easy the detection of VOCs with very low vapor pressure of saturation that are very difficult to be desorbed.

In addition, the adsorption capacity of the microporous silicon itself is not uninteresting since, due to its low desorption temperature, it could probably be directly used as adsorbent material for certain vapors such as nitrobenzene.

Moreover, we are currently studying the preconcentration of VOCs mixture by exploiting the difference of desorption between gases in order to separate their desorption peaks. In this case, the combining of porous silicon and other alternative materials seems an interesting way to improve the performance of our micro-preconcentrator.

5. REFERENCES

- [1] P. R. Lewis, R. P. Manginell, D. R. Adkins, R. J. Kottenstette, D. R. Wheeler, Recent Advancements in the Gas-Phase MicroChemLab. *IEEE Sensors Journal*, Vol. 6, N^o. 3, June 2006 pp 784-795.
- [2] I. Gràcia, P. Ivanov, F. Blanco, N. Sabaté, X. Vilanova, X. Correig, L. Fonseca, E. Figueras, J. Santander, C. Cané, Sub-ppm gas sensor detection via spiral micro-preconcentrator. *Sensors and actuators B* 132 (2008) pp 149-154.
- [3] A.M. Ruiz, I. Gracia, N. Sabate, P. Ivanov, A. Sanchez, M. Duch, M. Gerboles, A. Moreno, C. Cane, Membrane-suspended microgrid as a gas preconcentrator for chromatographic applications. *Sensors and Actuators A* 135 (2007) pp 192–196.
- [4] I. Voiculescu, R. A. McGill, M. E. Zaghoul, Micropreconcentrator for enhanced trace detection of explosives and chemical agents. *IEEE Sensors Journal*, Vol. 6, N^o. 5, October 2006 pp 1094-1104.
- [5] F. Zheng, D. L. Baldwin, L. S. Fifield, N. C. Anheier Jr., C. L. Aardahl, and J. W. Grate, Single-walled carbon nanotube paper as a sorbent for organic vapour preconcentration. *Anal. Chem.* 2006, 78 pp 2442-2446.
- [6] W.-C. Tian, H. K. L. Chan, C.-J. Lu, S. W. Pang and E. T. Zellers, Multiple-Stage Microfabricated Preconcentrator-Focuser for Micro Gas Chromatography System. *Journal of Microelectronical system* vol. 14, N^o 3, June 2005 pp 264-272.
- [7] G. Serrano, H. Chang, E. T. Zellers, A micro gas chromatograph for high-speed determinations of explosive vapors. *Proceeding of Transducers 2009 conference*, Denver, CO, USA, June 21-25, 2009 pp 1654-1657.
- [8] C. Lu, W. H. Steinecker, W.-C. Tian, M. C. Oborny, J. M. Nichols, M. Agah, J. A. Potkay, H. K. L. Chan, J. Driscoll, R. D. Sacks, K. D. Wise, S. W. Pang, E. T. Zellers, First-generation hybrid MEMS gas chromatograph. *The Royal Society of Chemistry, lab Chip* 5 (2005) pp 1123-1131.
- [9] S.-I. Ohira, K. Toda, Micro gas analyzers for environmental and medical applications. *Analytica Chimica Acta* 619 (2008) pp 143–156.
- [10] E. T. Zellers, K. D. Wise, K. Najafi, R. B. Brown, Q. J. Cai, J. Driscoll, Determination of complex vapor mixtures in ambient air with a wireless microanalytical system : vision, progress, and homeland

- security applications.. Technical Digest of the IEEE Conference on Technologies for Homeland Security, Waltham MA, USA, November 13-14, 2002 pp 92-95.
- [11] V. Gabelica, Intérêt de la spectrométrie de mobilité ionique pour l'étude de la conformation et des assemblages non-covalents de biomolécules. *Spectra Analyse* N^o. 251, Septembre - Octobre (2006) pp 21-27.
 - [12] H. Borsdorf, G. A. Eiceman, Ion Mobility Spectrometry: Principles and Applications. *Applied Spectroscopy Reviews*, vol. 41, N^o. 4 (2006) pp 323 -375.
 - [13] M. Martin, M. Crain, K. Walsh, R. E. McGill, E. Houser, J. Stepnowski, S. Stepnowski, H.-D. Wu, S. Ross, Microfabricated vapor preconcentrator for portable ion mobility spectroscopy. *Sensors and actuators B* 126 (2007) pp 447-454.
 - [14] K. Persaud and G. H. Dodd, Analysis of discrimination mechanisms in the mammalian olfactory system using a model nose. *Nature* 299 (1982) pp 352–355.
 - [15] X. Xu, F. Tian, S. X. Yang, Q. Li, J. Yan, J. Ma, A solid trap and thermal desorption system with application to a medical Electronic Nose. *Sensors*, 8 (2008) pp 6885-6898.
 - [16] F. Bender, N. Barié, G. Romoudis, A. Voigt, M. Rapp, Development of a preconcentration unit for a SAW sensor micro array and its use for indoor air quality monitoring. *Sensors and Actuators B* 93 (2003) pp 135–141.
 - [17] S. M. Cho, Y. Jun Kim, G. S. Heo, S-M. Shin, Two-step preconcentration for analysis of exhaled gas of human breath with electronic nose. *Sensors and actuators B* 117 (2006) pp 50-57.
 - [18] W. A. Groves, E. T. Zellers, G. C. Frye, Analyzing organic vapors in exhaled breath using a surface acoustic wave sensor array with preconcentration: Selection and characterization of preconcentrator adsorbent. *Analytica chimica Acta* 371 (1998) pp 131-143.
 - [19] United States Environmental Protection Agency: <http://www.epa.gov/>.
 - [20] Institut Français de l'Environnement : <http://www.ifen.fr/>.
 - [21] B. Alfeeli, M. Agah, Selective preconcentration by temperature manipulation of cascaded Micro preconcentrators. *Proceeding of Transducers 2009 conference*, Denver, CO, USA, June 21-25, 2009 pp 1662-1665.
 - [22] E.H.M. Camara, P. Breuil, D. Briand, C. Pijolat, N.F. de Rooij, A Micro Gas Preconcentrator with

improved performances for environmental monitoring. Proceeding of Transducers 2009 conference, Denver, CO, USA, June 21-25, 2009 pp 983-986.

- [23] E.H.M. Camara, P. Breuil, D. Briand, L. Guillot, C. Pijolat, N.F. de Rooij, "Micro gas preconcentrator in porous silicon filled with a carbon absorbent" [Sensors and Actuators B 148 \(2010\) pp 610–619](#).
- [24] C. Pijolat, M. Camara, J. Courbat, J-P. Viricelle, D. Briand, N.F. de Rooij, "Application of carbon nanopowders for gas micro-preconcentrator" *Sensors and Actuators B*, 127 (2007) pp 179-185.

FIGURES

Figure 1: Velocity cartographies obtained after a CFD simulation with microchannels in neural design without channel system at the inlet/outlet for a flow rate of 20L/h (a) and 40L/h (b) and in neutral (c) and zigzag (d) designs with channel system at the inlet/outlet for a flow rate of 20L/h.

Figure 2: Micro-channel in porous silicon filled with carbon with metallic gas capillaries and suspended in metallic box.

Figure 3: TPD spectrum of Carbon nanopowder after benzene adsorption.

Figure 4: TPD spectrum of Tenax polymer after benzene adsorption.

Figure 5: TPD spectrum of SWCNTs after benzene adsorption.

Figure 6: TPD spectrum of MWCNTs after benzene adsorption.

Figure 7: TPD spectrum of carbon nanopowder deposited on porous and non-porous silicon after benzene adsorption.

Figure 8: Comparison of gas sensor response between porous silicon and non porous silicon micro-channels filled with carbon nanopowder after an adsorption step of 250ppb and desorption step at 200°C with a heating rate of 160°C/min.

Figure 9: Sensor response for a silicon micro-channel filled with activated carbon nanopowder with and without humidity, when exposed to 5min to 250ppb of benzene and desorbed during 5min at a temperature of 200°C.

Figure 10: PID response of silicon micro-channel filled with SWCNTs with and without humidity when exposed to 5min to 250ppb of benzene and desorbed at 240°C.

Figure 11: TPD spectrum of Carbon nanopowder after nitrobenzene adsorption

Figure 12: TPD spectrum of Carbon Tenax polymer after nitrobenzene adsorption.

Figure 13: PID response of a silicon micro-channel filled with activated carbon nanopowder when exposed to 120min to 1ppm of nitrobenzene and desorbed at a temperature of 200°C.

Figure 14: PID response of a silicon micro-channel filled with Tenax TA when exposed to 45min to 1ppm of nitrobenzene and desorbed a temperature of 140°C.

Figure 15: Pressure and velocity cartographies obtained after a CFD simulation at 20 L/h with a new microchannel in neutral design.

TABLES

Table 1: Specific area and particle size of different adsorbents.

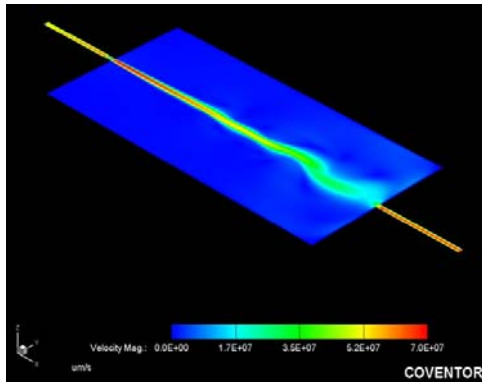
Table 2: Summary of results obtained with our micro gas preconcentrator according the adsorbent material, the preconcentrator substrate and the target gas. Symbols +++, ++, + and – mean respectively very good, good, medium and bad results

Adsorbent	Specific area (m²/g)	Particle size (μm)
Carbon nanopowder	99 +/-1	0.1
Activated carbon nanopowder	490 +/- 8	0.1
SWCNTs	399 +/- 5	2
MWCNTs	21 +/- 1	5
Tenax TA	35 +/- 2	250

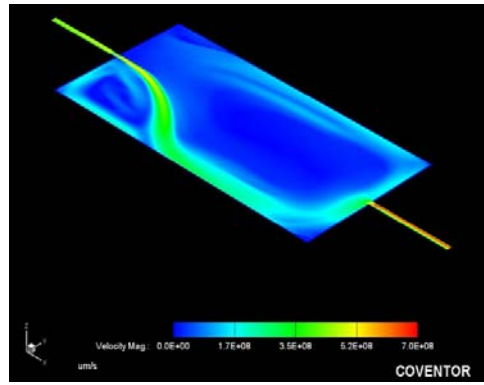
Table 1: Specific area and particle size of different adsorbents.

Gas →			
Adsorbent/Substrate ↓	Benzene	Xylene	Nitrobenzene
Carbon / Silicon	+++	++	—
Carbon / Macroporous silicon	+++	+++	NA
SWCNTs / Silicon	++	+	—
SWCNTs / Macroporous silicon	+++	+++	
Tenax TA / Silicon	++	++	++

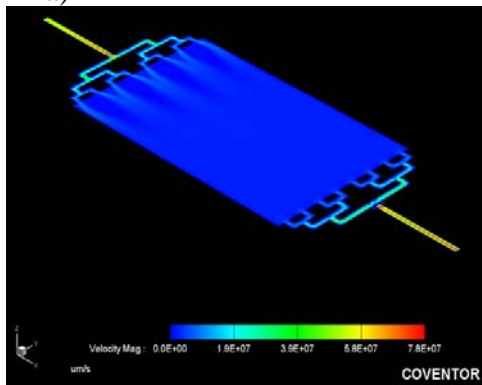
Table 2: Summary of results obtained with our micro gas preconcentrator according the adsorbent material, the preconcentrator substrate and the target gas, +++, ++, + and — mean respectively very good, good, medium and bad results, .



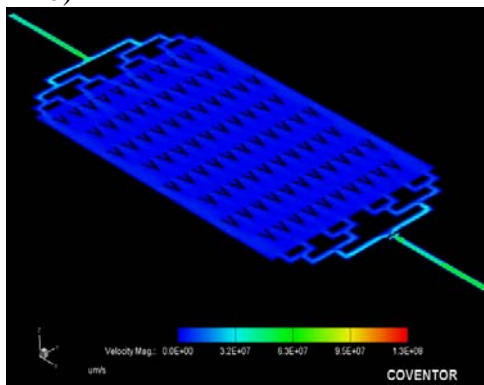
a)



b)



c)



d)

